

Origin of natural asphalt in Mercury deposit Merník, East Slovakia

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Abstract: During historical mining of cinnabar (HgS), an association of organic minerals, ozokerite and natural asphalt was identified. The occurrence of these solid hydrocarbons has been attributed to the presence of organic matter rich Neogene sediments of Karpatian and Badenian age exposed along the periphery of the Slanské vrchy Mountains. Thermal alteration of organic matter and subsequent hydrocarbon migration were most likely induced by elevated temperatures associated with intrusive magmatism and related hydrothermal processes. This study aims to evaluate the origin of the natural asphalt using detailed organic geochemical analyses (GC, GC–MS). Potential source rocks were evaluated based on the vertical and lateral distribution of sediments of the Central Carpathian Paleogene Basin (CCPB) in the Lipany-1 well area and, in the Prešov-1 well area, also of Lower Miocene sedimentary units. These successions were characterized using standard organic geochemical parameters, including total organic carbon (TOC), kerogen type, and thermal maturity indicators. Thermal maturity modeling of the CCPB sedimentary succession was performed and compared with measured vitrinite reflectance (Ro) data, which indicate that parts of the basin reached the oil window. The potential source to Merník asphalt relationship was evaluated based on steranes and triterpanes correlations. The biomarker data demonstrate that the natural asphalt from the Merník locality is genetically related to organic matter within the CCPB sediments. In contrast, nearby Lower Miocene sedimentary rocks in the northern part of the andesitic stratovolcano did not reach the sufficient thermal maturity for hydrocarbon generation and can therefore be excluded as effective source rocks.

Key words: East Slovakia, neovolcanics, rhyodacites, asphalt, source rocks, GC–MS correlations

1. INTRODUCTION

Within the cadastral territory of the Merník village in eastern Slovakia, an abandoned mercury ore deposit is located (Fig. 1), where mining and ore processing were carried out over a long term period. According to archival records, the beginnings of mercury mining date back to the 17th century and continued until 1937. After the cessation of mining activities, several attempts were undertaken to quantify the remaining reserves of the deposit within the framework of various geological investigation and exploration programs.

Geological studies with reserve calculations carried out in the second half of the 20th century (Bačo et al., 1988; Repčiak, 1994) did not yield the expected results. Therefore, further exploitation of the deposit particularly in terms of reserve quantity, ore quality, world market prices, extraction, transport, and processing costs, as well as ecological considerations was no longer feasible (Daniel et al., 2003). As a result of mining and ore-processing activities, a concentration of waste dump material has remained at the site. Erosion, dispersal, and leaching of the dumps by surface water represent a potential source of contamination of the surrounding environmental components, primarily with risk elements of geogenic origin such as mercury, antimony, and nickel, as well as with substances typical of mining areas, namely Fe, Mn, and sulfates, which are comprehensively evaluated in the work of Jurkovič et al. (2016).

It is generally well established that volcanogenic polymetallic, and particularly mercury, deposits structurally and genetically related to Tertiary volcanism are often accompanied by an association of organic minerals, ozokerite, and asphalt. The

occurrence of such an association was documented many years ago in close spatial relation to hydrothermal mineralization within the Zlatobanský andesitic stratovolcano in the northern part of the Slanské vrchy Mountains (Fig. 1). The processes resulting in polymetallic, low-temperature Sb–Hg–As and opal mineralization are linked to the intrusive–hydrothermal activity of the stratovolcano. The identified organic minerals in the near-surface zone occur predominantly in the form of small veins or fracture fillings, nests, and impregnations within rock pores, frequently in paragenesis with low-temperature carbonates, chalcedony, zeolites, and related minerals.

The position of these organic mineral occurrences, as well as their close spatial association with the products of hydrothermal mineralization, provides several possibilities for interpreting their genesis. This contribution primarily presents the geochemical characterization of natural asphalt and its probable source, along with the potential source of the organic minerals, that is, the original source rocks, based mainly on the study of biomarkers in the context of the geological structure of the surrounding area.

2. GEOLOGICAL CHARACTERISTICS OF THE DEPOSIT AND ITS WIDER SURROUNDINGS

The Merník deposit is situated within the northern marginal zone of the East Slovak Neogene Basin (Fig. 2). The deposit itself lies on the south–southwestern margin of the CCPB, approximately 4 km east of the volcanic Slanské vrchy Mountains, in close proximity to the Močarany–Topľa fault system, which is intersected by faults trending NNE–SSW.

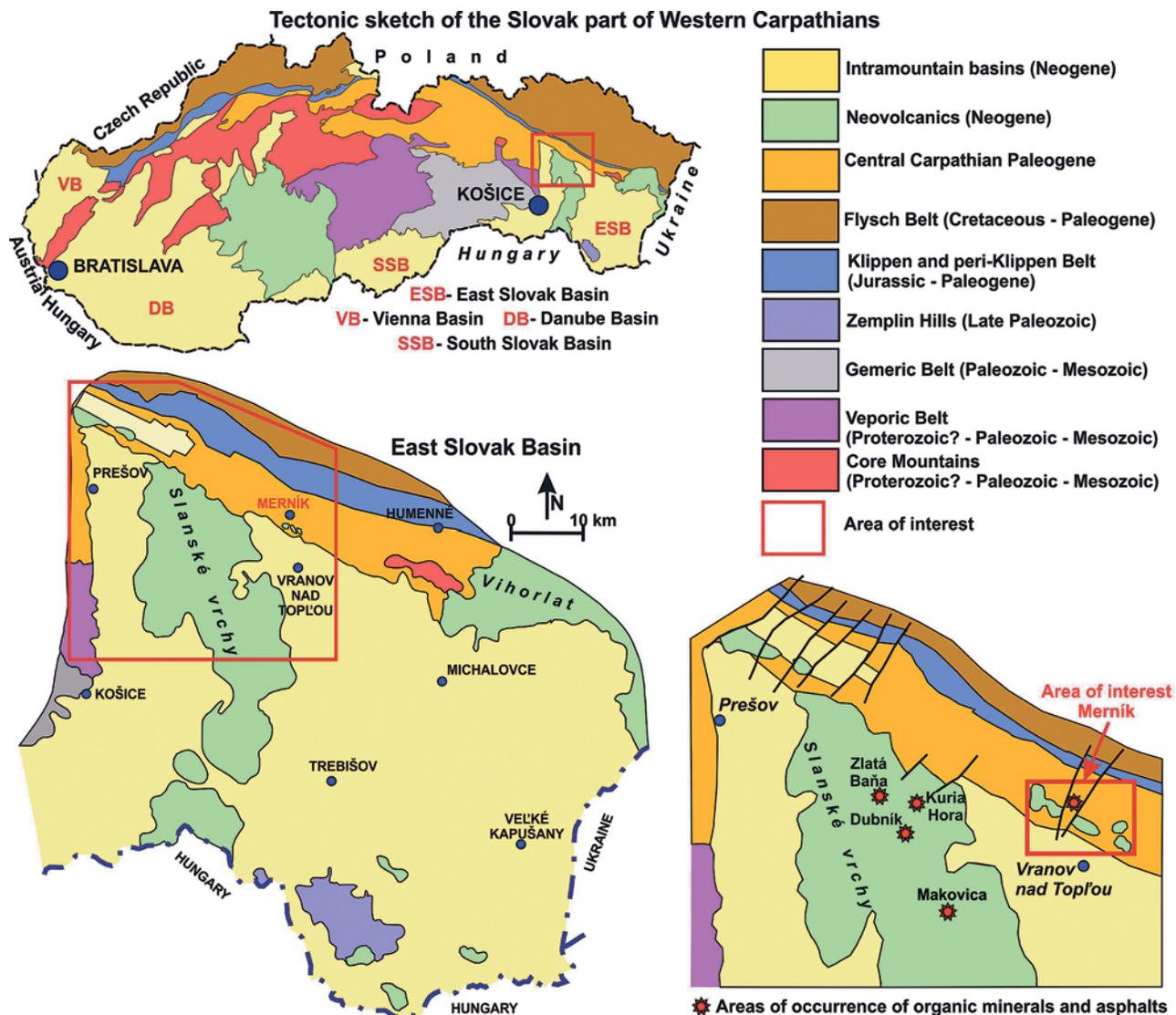


Fig. 1: Position of the study area within the Western Carpathians in Slovakia (modified from a general geological map of Slovakia – <https://app.geology.sk/pgm/>)

Quaternary: 1 – gravels, sands, loams, Neogene: 2 – undivided volcanic rocks of the Slanské vrchy Hills (Badenian – Pannonian), 3 – intrusions and extrusions of rhyodacites (Upper Badenian), 4 – undivided molasses of the East Slovak Basin (Egerian – Lower Sarmatian), Paleogene: 5 – flysch with a predominance of claystones to siltstones, 6 – intraformational Merník conglomerates, Mesozoic: 7 – Krížna nappe (limestones, dolomites, marls - Humenské unit), 8 – supposed faults, 9 – geological profile – fig. 3, 10 – area of interest

The deposit area is composed of the CCPB sediments, intruded by a system of rhyodacitic bodies in the form of stocks and dikes of Badenian to Lower Sarmatian age. The oldest complex exposed at the surface in the form of isolated islands from the CCPB in the broader vicinity of the deposit is the Humenné Unit, consisting of Mesozoic rocks of the Krížna Nappe (Maheľ, 1984). The Mesozoic sequence is represented by Triassic limestones and dolomites. In some places, dark-gray marly limestones, marlstones, and sandy marlstones of Jurassic and Lower Cretaceous age also crop out (Fig. 3).

Neogene: 1 – undivided volcanic rocks of the Slanské vrchy Hills (Badenian – Pannonian), 2 – intrusions and extrusions of rhyodacites (Upper Badenian), 3 – undivided molasses of the East Slovak Basin (Egerian – Lower Sarmatian), Paleogene: 4 – flysch with a predominance of claystones to siltstones, 5 – intraformational Merník conglomerates, Mesozoic: 6 – Krížna nappe (limestones, dolomites, marls - Humenské unit), 7 – supposed faults, 8 – area of interest

On the pre-Tertiary basement lie transgressive sediments of the CCPB (Eocene) with characteristic formations. In the basal Borové Formation, beds of coarse-grained conglomerates and breccias alternate with beds of sandstones. The clastic material is composed mainly of Mesozoic rocks. The overlying the sediments exhibit a flysch character - the Huty Formation with a predominance of claystones and the Zuberec Formation with a predominance of sandstones (Gross et al., 1984). Both formations contain interbeds of intraformational conglomerates and breccias, the so-called Merník conglomerates, which locally reach thicknesses of up to 280 m (Bačo et al., 1988). Soták et al.

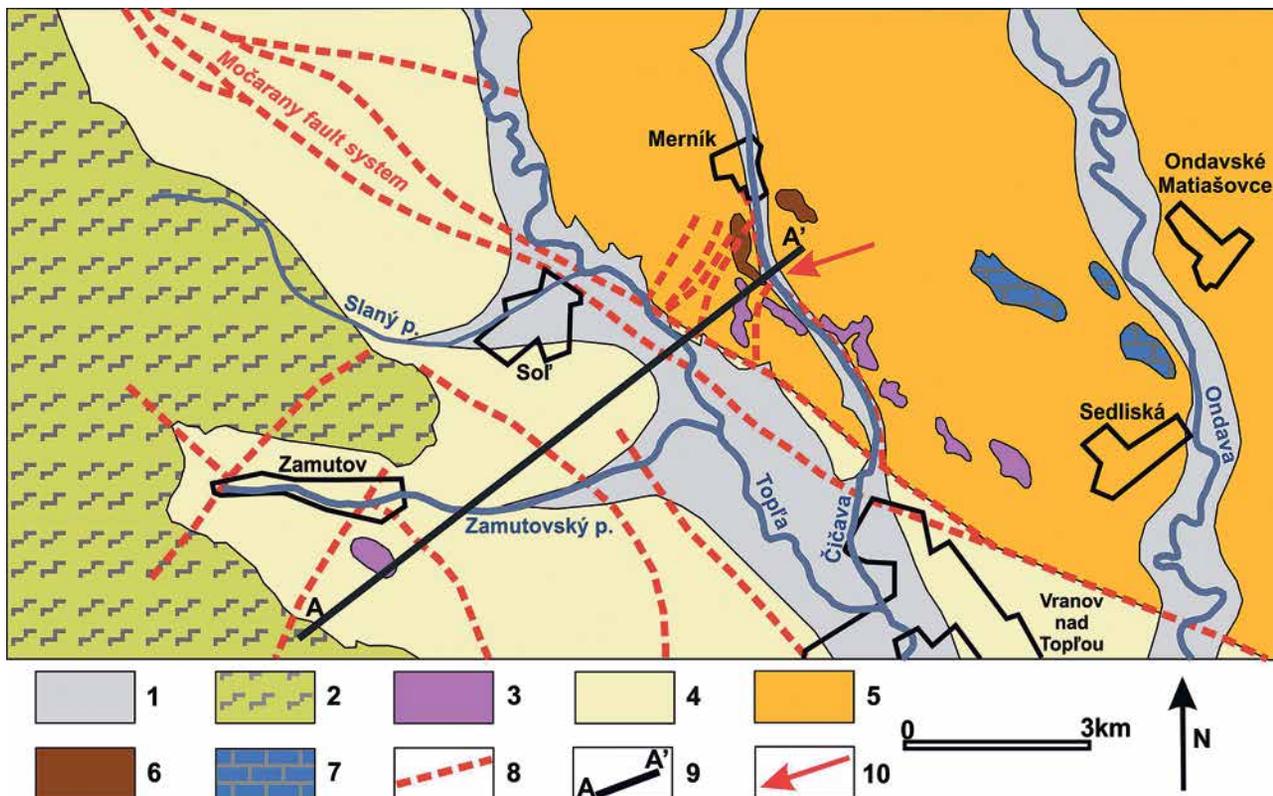


Fig. 2: Geological map of a wider area of interest (adapted from Bačo et al., 1988)

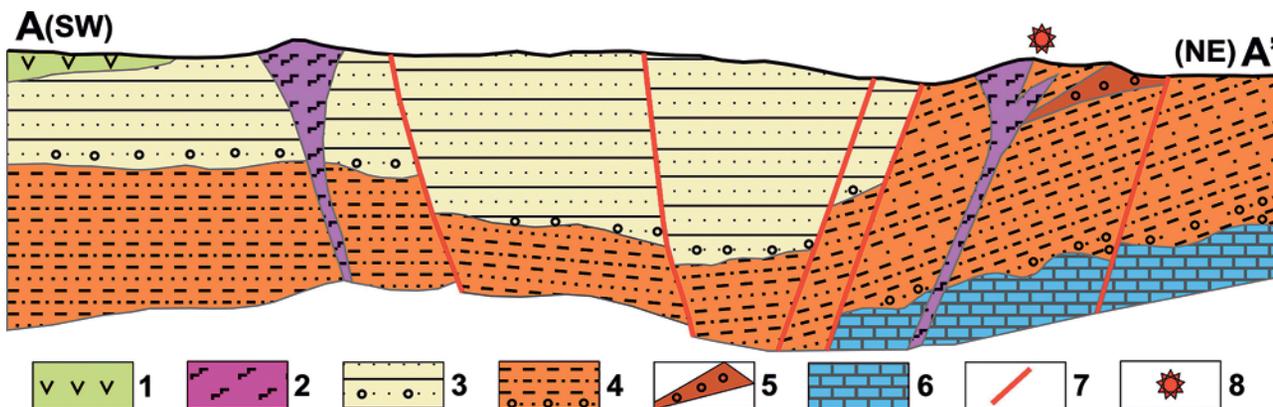


Fig. 3: Simplified profile through the area of interest (adapted from Bačo et al., 1988)

(1991) report a thickness of up to 150 m for the conglomerate cycle. The uppermost sandy Biely Potok Formation, if developed, occurs only in minor relics.

In the broader area of the deposit, Neogene sediments and volcanics of the East Slovak Neogene Basin overlie transgressively the Paleogene rocks, or directly on the pre-Tertiary basement. Individual Neogene formations, their lithological composition, and descriptions are depicted in Fig. 4.

Neogene: 1 – Stretava Formation (Lower – Middle Sarmatian) – clays, claystones, 2 – Klčovo Formation (Upper Badenian) – sandstones, shales, intrusive rhyodacites and extrusive andesites, 3 – Lastomír Formation (Upper Badenian) – calcareous clays, shales, sandstone intercalations, 4 – Zbudza Formation (Middle Badenian) – evaporites, saline clays, 5 – Vranov Formation (Middle Badenian) – siltstones, shales, sandstones,

6 – Nižný Hrabovec Formation (Lower Badenian) – sandstones, shales, rhyodacite tuffs, 7 – Kladzany Formation (Upper Karpatian) – variegated claystones, sandstones, 8 – Soľná Baňa Formation (Middle Karpatian) – saline clays, sandstones, 9 – Teriakovce Formation (Lower Karpatian) – sandstones, shale, conglomerates, 10 – Prešov Formation (Eggenburgian) – shales, calcareous sandstones, Paleogene: 11 – Biely Potok Formation (Upper Priabonian) – sandstones, claystone and conglomerate intercalations, 12 – Zuberec Formation (Middle Priabonian) – sandstones, claystones, 13 – Huty Formation (Lower Priabonian) – claystones, 14 – Borové Formation (Middle – Upper Lutetian) – sandstones, conglomerates, limestones, 15 – intraformational conglomerates, Mesozoic: 16 – Krížna Nappe (Humenné Unit) – limestones, marly limestones, marlstones, dolomites, 17 – Crystalline: unproven – presumed.

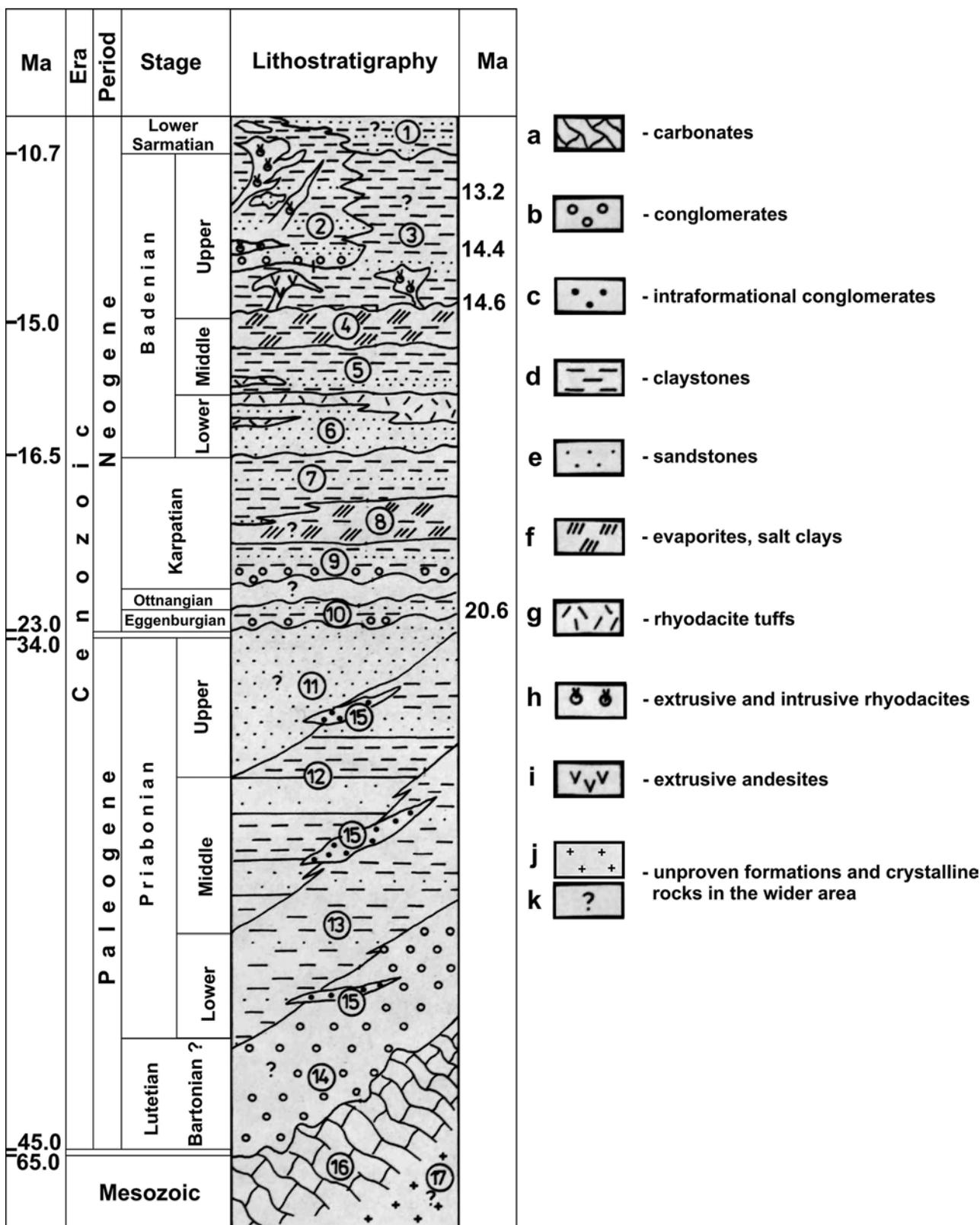


Fig. 4: Lithostratigraphic scheme of the wider surroundings of the Merník mercury deposit (adapted from Bačo et al., 1988).

An important geological factor in the area of the deposit and its surroundings was the Neogene volcanism and the associated hydrothermal and metallogenetic processes. The products of volcanism of both extrusive and intrusive character are assigned to the age of Badenian to Lower Sarmatian (Kaličiak & Repčok,

1987). Extensive rhyolitic volcanism took place during the Lower Badenian age. In the period from the Upper Badenian to the lowermost Sarmatian, besides rhyolitic volcanism, the first significant andesitic volcanism is also documented. The most prominent volcanic activity occurred in the Sarmatian, when the stratovolcanic

structures of the Slanské vrchy were formed. These are composed predominantly of intermediate volcanics, but also include rhyolitic volcanism. In the Lower Sarmatian volcanoclastics are dominant (Bačo et al., 1988). During the Pannonian, volcanism in the East Slovak Neogene Basin gradually subsided and ceased.

Quaternary sediments in the deposit area are represented by redeposited weathering products of variable thickness. These are mainly stony and clayey-stony slope deposits and fluvial sediments.

In the geological structure of the wider Merník deposit area, the most significant role is played by the so-called Močarany–Topľa fault system of NW–SE orientation with a SW dip, along which Paleogene sediments are in contact with the Neogene basin fill. The main faults of this system were syndimentary with respect to the Badenian and Sarmatian sediments. However, transverse faults of NE–SW orientation played an important role in the formation and localization of mineralization. Almost

all occurrences and indications of mercury ores and organic minerals known so far in the wider vicinity of the deposit are associated mainly with rhyodacitic bodies (Figs. 5 and 6). These are controlled by the NW–SE fault system, especially at the intersections with transverse faults. Along these systems and through the surrounding environment, hydrothermal solutions were likely supplied from greater depths into the sites of mineral occurrences. The deposition of the contents of these solutions took place in lithologically favorable environments, predominantly in rhyodacites (Bačo et al., 1988). The structural and tectonic conditions in the broader area of the deposit are shown in Fig. 5.

3. MATERIALS AND METHODS

At present, two samples of natural asphalt are available, one collected from a mining tunnel in the Anna gallery (85 m

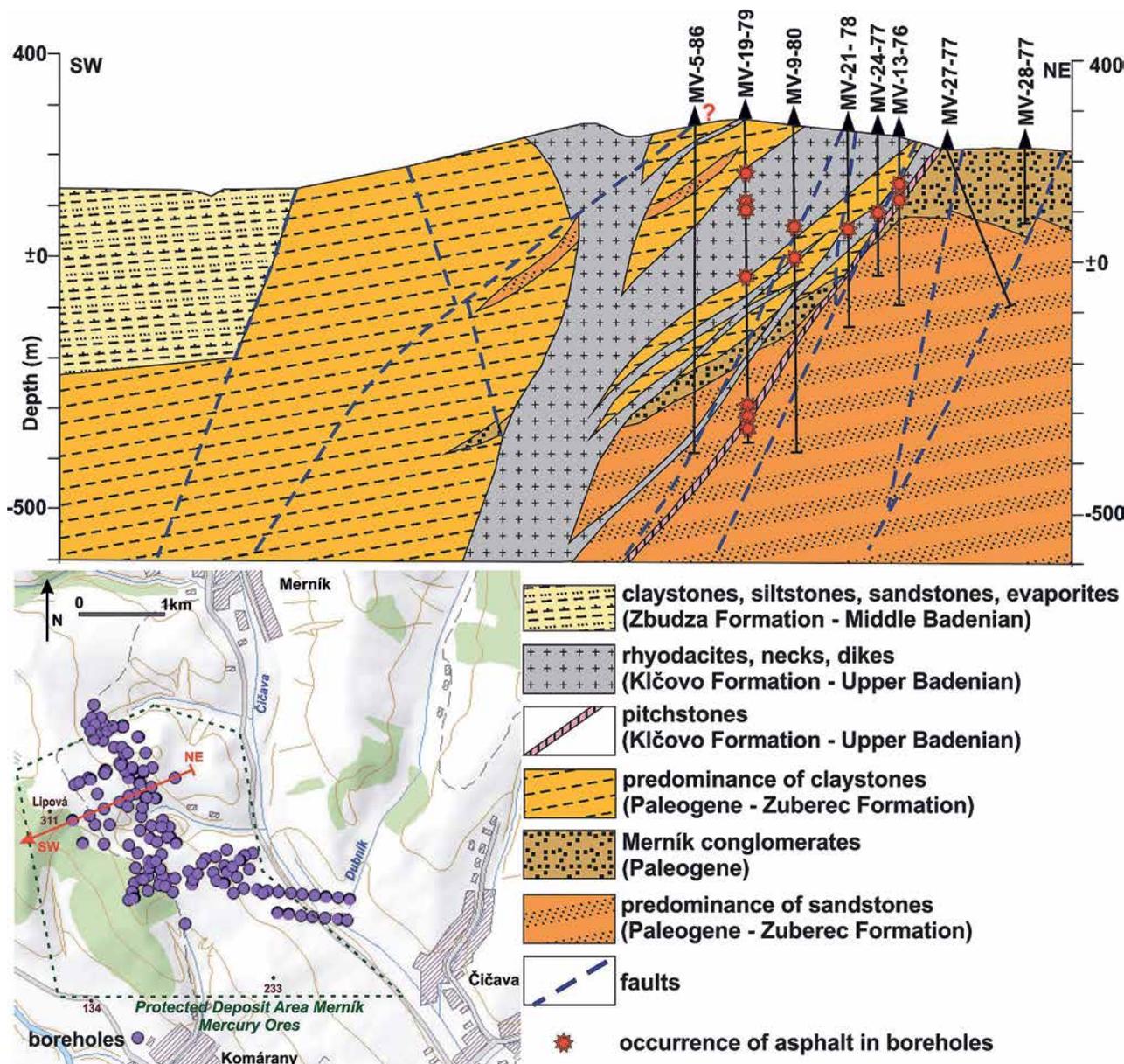
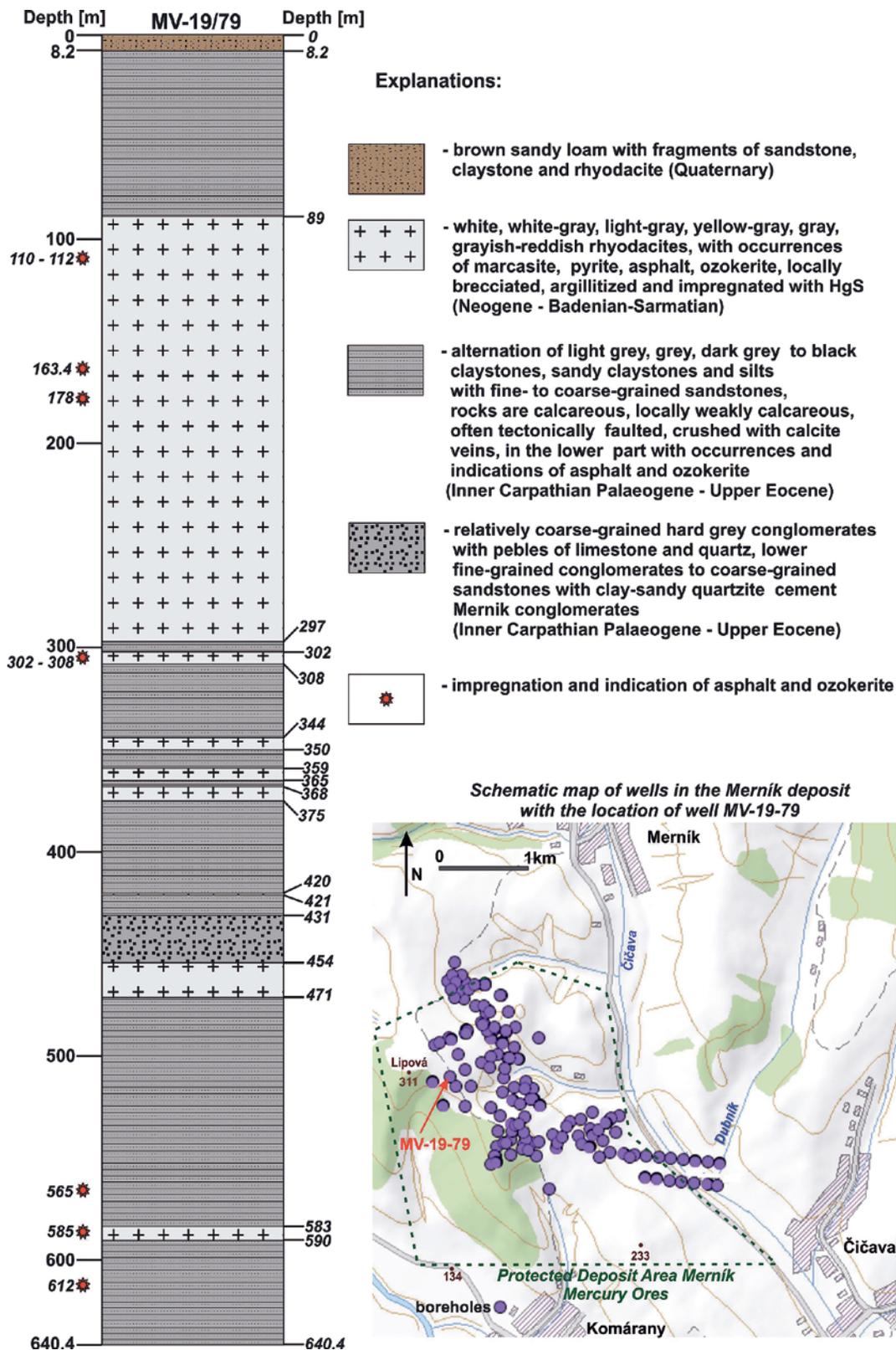


Fig. 5: Geological profile of the Merník mercury deposit boreholes with marking of asphalts occurrence in individual boreholes (adapted from Bačo et al., 1988)

Fig. 6: Detailed geological profile of borehole MV19/79 with marking of asphalt occurrence (adapted from Bačo et al., 1988)



representing older material, and a freshly collected sample from rhyodacite debris. The results presented here are derived from the analysis of the older sample obtained from the mining tunnel.

The analyses were carried out at the Czech Geological Survey (CGS), Prague, branch Brno (elemental analysis, Rock-Eval pyrolysis, GC, and GC-MS).

3.1 Elemental Analysis

This analysis provides an overview of the elemental chemical composition of the investigated samples, with particular emphasis on the contents of the biogenic elements C, O, H, N, and S, and thus on the compositional characteristics of the original

organic matter from which they were derived. The analyses were performed at the Czech Geological Survey (CGS), Prague, using the standard methodology applied at the Brno branch. The results are presented in Table 1.

3.2 Gas Chromatography (GC)

Gas chromatography of the aliphatic fraction of the chloroform extract was performed at the Czech Geological Survey (CGS), Prague, using the standard methodology applied at the Brno branch. Prior to analysis, the extract was separated into aliphatic and aromatic fractions and NSO compounds (Table 1); the aliphatic fraction was subsequently analyzed (Fig. 8).

3.3 Gas Chromatography–Mass Spectrometry (GC-MS)

The principal method for detailed characterization of the molecular composition of the asphalt and for correlation the Merník asphalts with their original kerogen source was GC–MS analysis. The analyses were carried out at the Brno branch of the Czech Geological Survey (CGS) under following conditions:

The extract was separated into individual fractions. The aliphatic and aromatic fractions were adjusted to appropriate concentrations and analyzed using a Hewlett-Packard HP 5998A GC/MS system equipped with a 60 m capillary column (internal diameter 0.25 mm, stationary-phase film 0.25 μm thick). Helium was used as the carrier gas at a pressure of 160 kPa. The analyses were performed in SIM mode on several diagnostic fragment ions; for interpretation, the most important fragments were m/z 218 and m/z 191. The results are presented in Table 2 and Figure 9.

3.4 Modeling of the geological history and thermal maturity of organic matter

Modeling of the geological and thermal history of a given locality represents a way of obtaining information on the maturity of organic matter in both temporal and depth-related contexts. Basin modeling software is based on a comprehensive understanding of the mechanisms of sedimentary basin evolution. In particular, data and knowledge from sedimentology, litho- and chronostratigraphy, paleogeography, paleoclimate, paleobathymetry, seismic surveys, well logs, thermophysical properties of sediments, organic geochemistry, and related disciplines are considered. These inputs control the modeling of subsidence rates, sediment compaction, paleotemperatures, paleowater depths, paleothermal flow mechanisms, as well as the amount, quality, and distribution of dispersed organic matter.

Input data for the software are of two types: optimization parameters, which can be adjusted, and control parameters. Optimization parameters are used together with calculated parameters to test and refine the conceptual model. Control parameters must be selected so as to be independent of the optimization parameters.

Input parameters that may simultaneously serve as optimization parameters include, for example, the type of event (deposition, hiatus, erosion, thrusting), duration of the event, lithology

of the sedimentary complex deposited at a given time, thickness of the complex, average porosity, water depth during sedimentation, paleotemperatures, and paleothermal heat flow. Control parameters may include present-day measured equilibrium temperatures, measured vitrinite reflectance, sterane and/or hopane isomerization ratios, and similar maturity indicators.

The most important aspect of such software is that it treats sedimentary basin modeling as a geological problem. Geological parameters are entered into the software in a step-by-step manner, i.e., as a sequential reconstruction of the sedimentary basin evolution in time and space. Time is the principal controlling factor to which all parameters, processes, and products are related.

Based on the input optimization parameters, the software constructs a model of sedimentary basin evolution, including the burial history of sediments, hydrocarbon generation windows, and related processes. In addition, it calculates theoretical vitrinite reflectance and theoretical present-day equilibrium temperatures. These theoretical results are compared with laboratory-determined vitrinite reflectance values and

measured temperatures. The input (optimization) parameters are iteratively adjusted until an acceptable agreement is achieved between the theoretically calculated and measured (control) parameters. At this stage, the model can be regarded as a reasonably realistic representation of the geological reality.

The hydrocarbon potential of the Miocene and Paleogene sediments in the broader study area was evaluated on the basis of models of the deep wells Lipany-1 and Prešov-1, which were modeled using the PetroMod software (Figs. 12 and 13).

3.5 Method for calculating of resources

For the calculation of resources of Paleogene sediments in the Lipany-1 well area, as well as in the Paleogene and Lower Miocene sediments in the Prešov-1 well area, the quantitative genetic method of Waples (1985) was applied. This method has been used in previous studies in various regions (Pereszlényi et al., 1995, 1996, 2002). The results are presented in Table 3.

4. RESULTS AND DISCUSSION

4.1 Geochemical characteristics of natural asphalt from Merník

In the studied area, the occurrence of solid bitumens - ozokerite and natural asphalts - was described in the past in connection with cinnabar mining. These occur as small droplets as well as larger accumulations of black, viscous asphaltic material filling fractures within rhyodacite veins (Kuthan, 1941). According to Slavík (1974), a yellowish-brown, partially semi-fluid amorphous asphaltic material also occurs sporadically in ore veins, in a paragenetic association with cinnabar. Ďuďa and Tözser (1978) referred to this material as "oil droplets." Based on the descriptions of the above-mentioned authors, ozokerite (also known as earth wax) is understood as a natural organic substance composed of a mixture of hydrocarbons, most commonly occurring as a waxy material in various color varieties.

Occurrences of natural asphalt, together with more recent comprehensive knowledge of the hydrocarbon potential of the Western Carpathians (Pereszlényi et al., 1996), provided the impuls for investigating the relationship between the Merník asphalt and potential petroleum source rocks.

At present, it is practically impossible to obtain an authentic sample from the ancienit deposit within the underground mine works, however, redeposited material, for example in slope debris, can still be found. A detailed description of asphalt occurrences (as well as ozokerite, earth wax, and “oil droplets”) is given in the report by Križáni (1985). According to the authors’ descriptions, during the period of active mining the occurrences of asphalt were mainly associated with horizons of fine- to medium-grained conglomerates and coarse-grained sandstones, and they also commonly occurred along fractures in rhyodacites.

From an analytical perspective, the geochemical characterization presented here is based on the study of a representative archival sample of natural asphalt collected from a mining tunnel in the Anna gallery at a depth of 85 m. As shown in Fig. 7, the asphalt occurs as a dark brown to black viscous cement and/or as coatings along fractures in rhyodacites. It is readily soluble in CHCl₃ at room temperature, the resulting extract is black and turbid.

In terms of elemental composition, the asphalt is predominantly composed of carbon and hydrogen atoms, with the remainder consisting of heteroatoms (N, S, O). Regarding hydrocarbon fractions, it contains the highest portion of aromatic hydrocarbons and polar NSO compounds (Table 1).

Tab. 1: Elemental analysis and extract fraction composition of Merník asphalt. Ali – aliphatic; Aro – aromatic fraction; NSO – polar compounds.

Elemental analysis					Hydrocarbon fractions		
C	H	N	S	O	ALI	ARO	NSO
75.89 %	8.33 %	1.37 %	1.81 %	12.60 %	22 %	42 %	36 %

The GC profile provides evidence of a high degree of biodegradation, the distribution of n-alkanes and the corresponding

isoprenoids is difficult to distinguish. Nevertheless, it contains a significant amount of biomarkers, observed as a pronounced increase (“hump”) in the right side of the chromatogram (Fig. 8).

Biomarker analysis (GC–MS) revealed a high portion of oleanane in the asphalt (oleanane index 0.73; Moldowan et al., 1994), indicating a Tertiary petroleum origin with a significant contribution of terrestrial plant material to the marine sedimentary environment. The mixed terrestrial–marine origin of the kerogen is further confirmed by

the relatively balanced distribution of C₂₇ steranes, indicative of a marine environment, and C₂₉ steranes, derived from higher plants (Table 2; Fig. 9)

Tab. 2: Indexes of steranes and triterpanes. Ts - 18α(H)-22,29,30 Trisnorneohopane; Tm: - 17α(H)-22,29,30 Trisnorhopane; Ol: Oleanane; Ho:

C30 Hopane.		
m/z	Index	
218	%27	37.68
218	%28	26.09
218	%29	36.23
191	Oleanane	52.94
191	C30 Hopane	19.61
191	Ol/Ol+Ho	0.73
191	Ts	96.08
191	Tm	109.80
191	Ts/(Ts+Tm)	0.47

During the exploratory investigation of ore deposits in the East Slovak Neovolcanites, organic minerals were also identified and described in the northern part of the Slanské Vrchy Hills and at the Merník deposit (Ďuďa et al., 1977; Ďuďa &

Tözsér, 1978; Ďuďa et al., 1981; Ďuďa & Kaličiaková, 1987). From this assemblage occurring in the northern Slanské Vrchy Hills, only idrialite from the Merník locality was available (Fig. 10).



Fig. 7: Asphalt coatings on rhyodacite, Merník

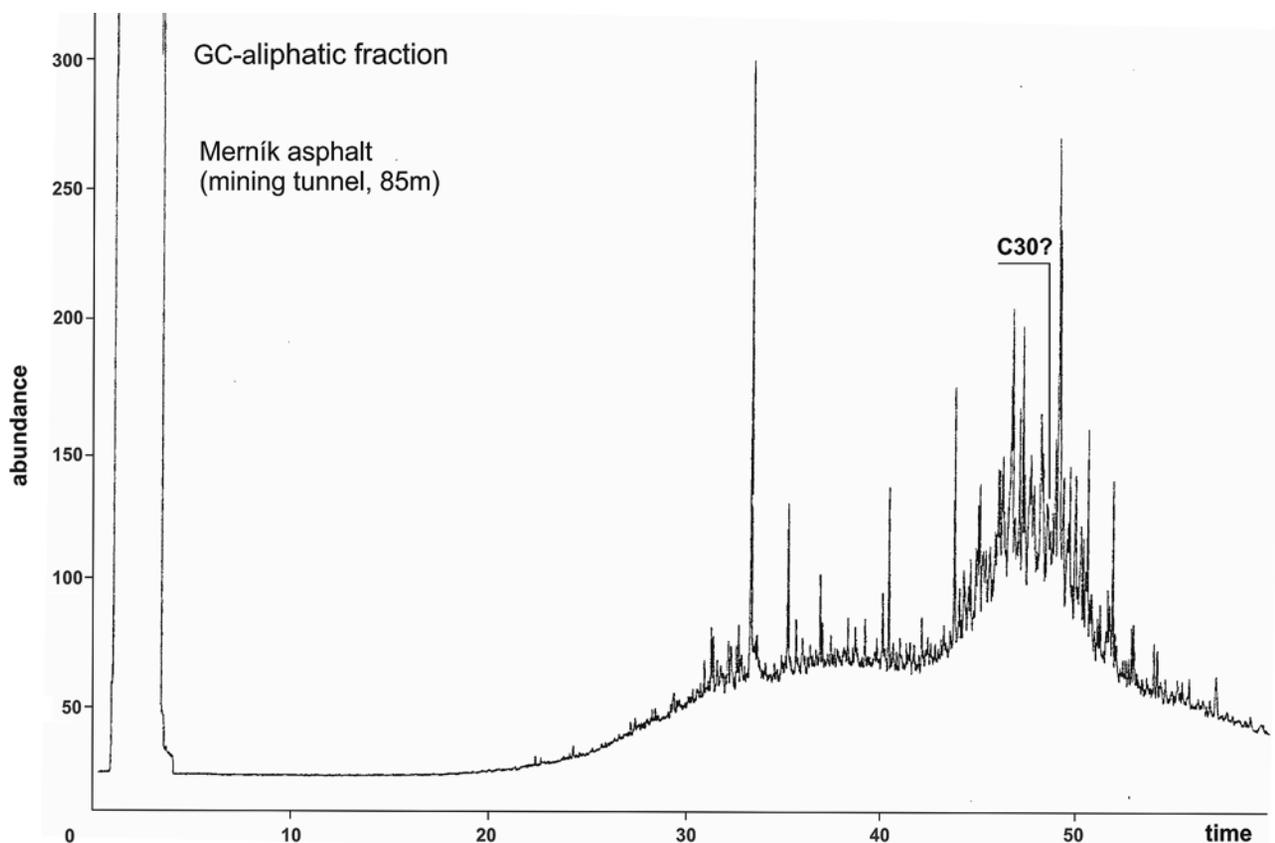


Fig. 8: Distribution of aliphatic hydrocarbons in Merník asphalt extract; C30?: possible position of 30 hopane

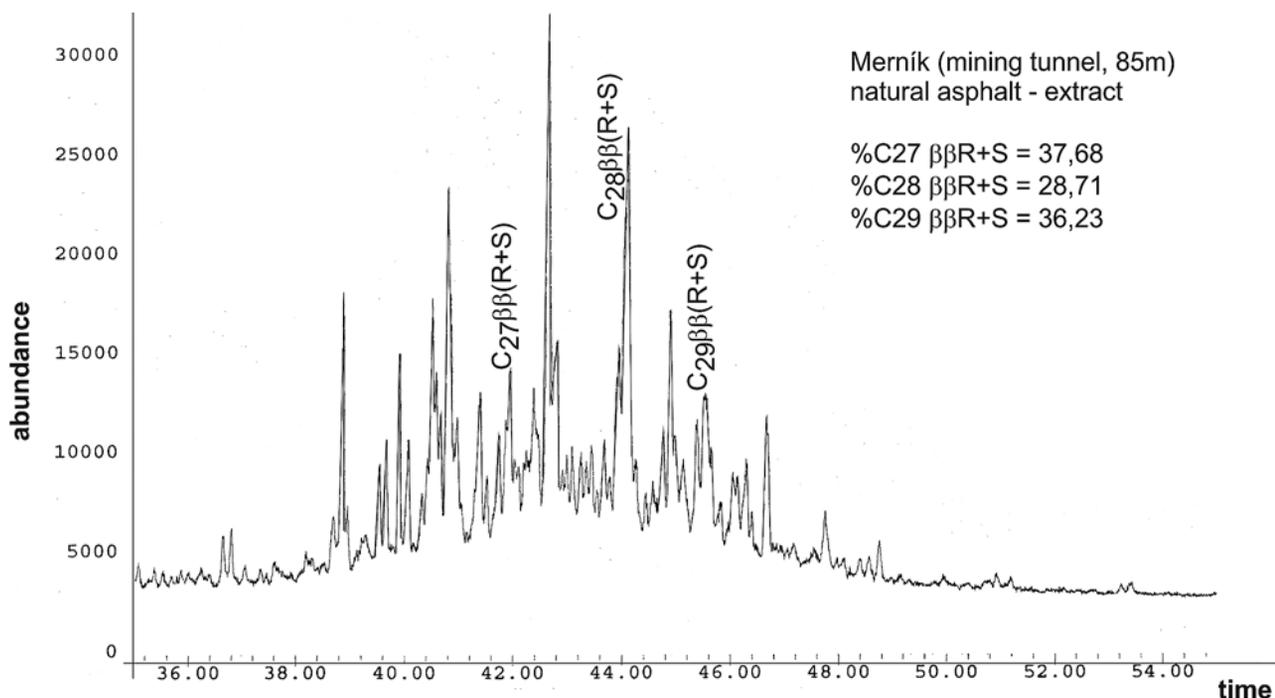


Fig. 9: Distribution of stranes (m/z 218) in extract of Merník asphalt.

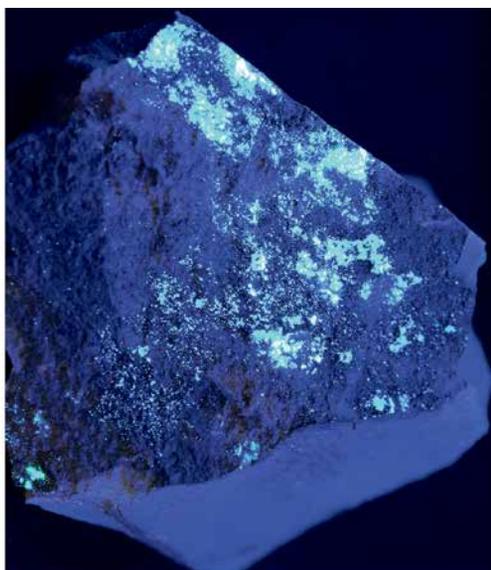
4.2 Hydrocarbon potential of adjacent Paleogene and Neogene sediments

As a source of organic matter from which petroleum and, subsequently, asphalt could potentially have originated at the

Merník locality, two types of source rocks are relevant in terms of the geological structure of the broader area: sediments of the Central Carpathian Paleogene Basin and Lower Miocene sediments. These sediments have been previously studied for their hydrocarbon potential using both routine and special



a

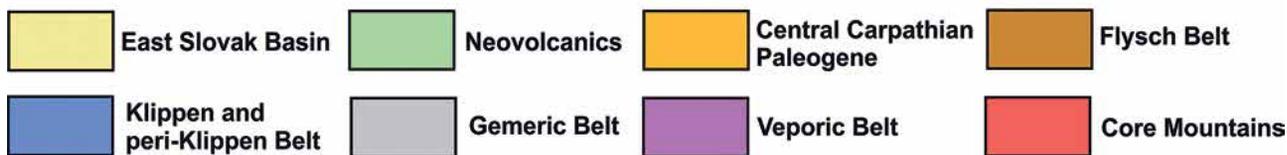
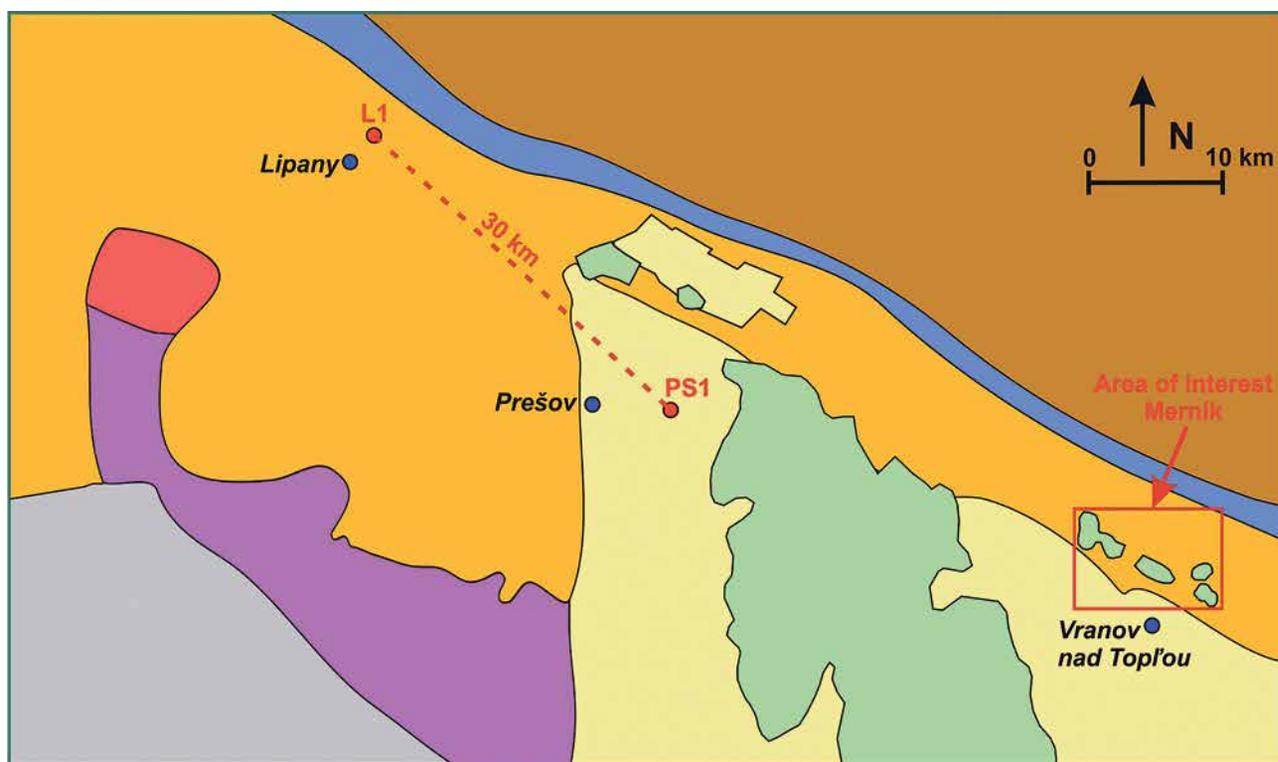


b

Fig 10: a/ Light green crystals of idrialite (C₂₂H₁₄) on rhyodacite., Merník; b/ Idrialite fluorescence under ultraviolet excitation ($\lambda \sim 365$ nm)

organic-geochemical methods, with results published in several articles and research reports (e.g., Pereszlényi et al., 1996; Soták et al., 2001; Pereszlényi et al., 2002; Milička & Pereszlényi, 2005; Pereszlényi & Milička, 2005).

To assess the hydrocarbon potential of the Miocene and Paleogene sediments in the broader study area (Fig. 11), models of the deep wells Lipany-1 and Prešov-1 are presented, which were constructed using the PetroMod software (Figs. 12 and 13).



Modeled wells: L1 Lipany 1 PS1 Prešov 1

Fig. 11: Location and distances of modeled wells Prešov 1 and Lipany 1

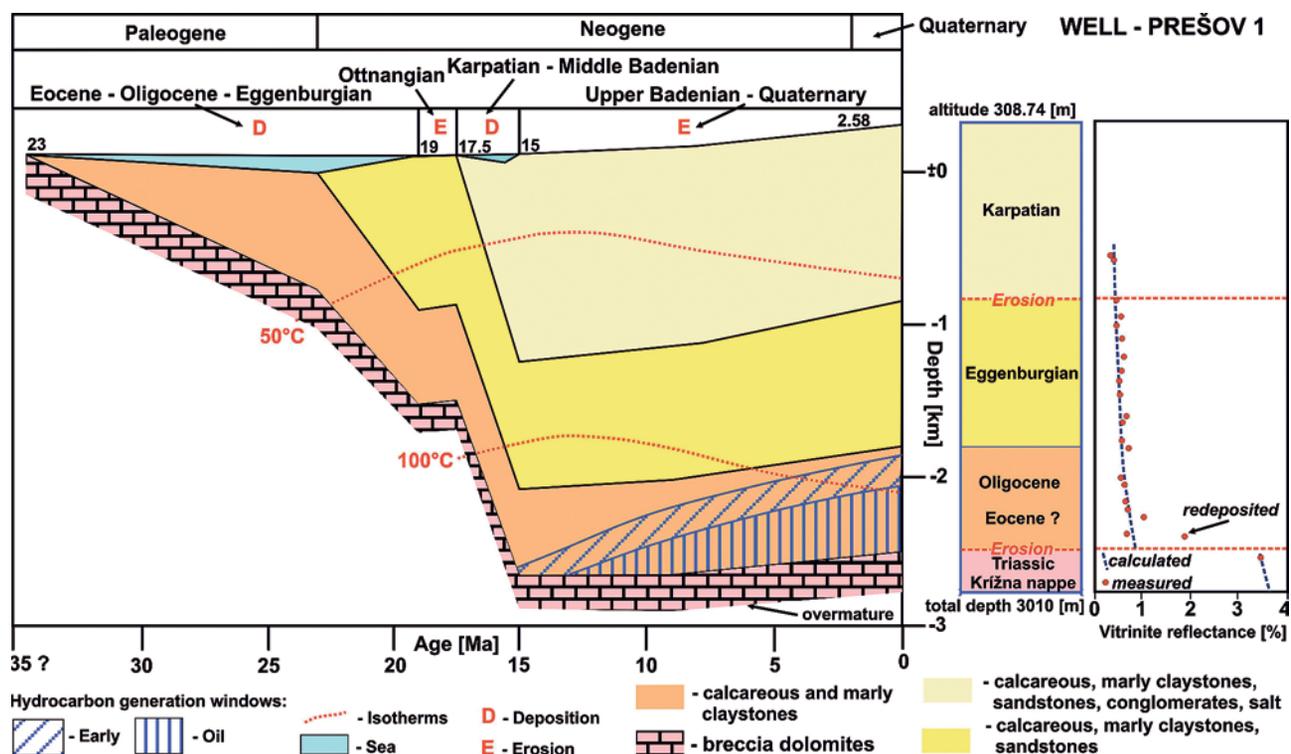


Fig. 12: Modeling of burial history of sediments and development of hydrocarbon generation windows at the Lipany 1 well.

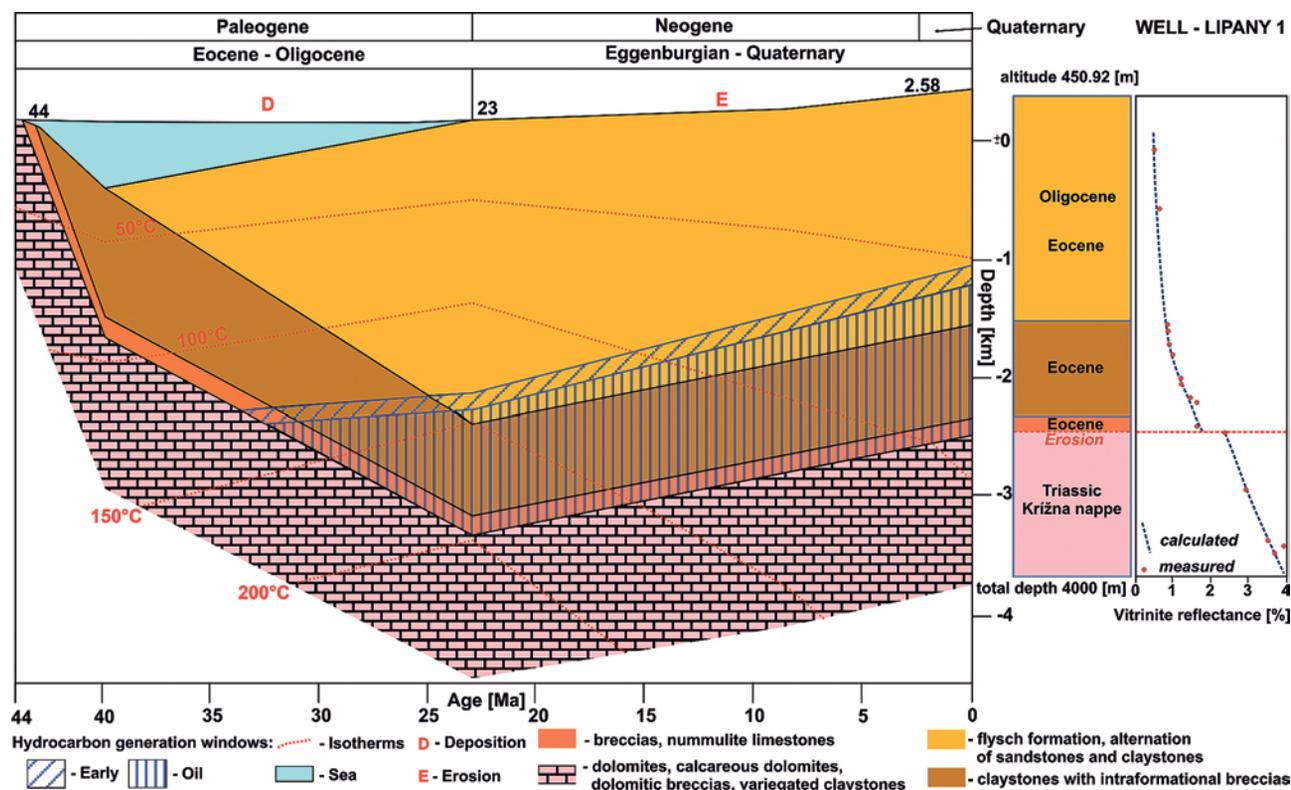


Fig. 13: Modeling of burial history of sediments and development of hydrocarbon generation windows at the Prešov 1 well.

The calculation of hydrocarbon volumes in a given geological region is based on dividing the process of hydrocarbon accumulation into several phases: generation, expulsion, migration, trapping in reservoirs, and preservation.

The hydrocarbon generation formula utilizes three

fundamental organic-geochemical parameters: the average total organic carbon (TOC) content and the hydrogen index (HI) values within the individual hydrocarbon generative zones.

Volume of hydrocarbons (HC) = (k) x (TOC) x (HI) x (f), where:

HC – hydrocarbon volume (million m³ per km³)

k – conversion constant of kerogen (0,7)

TOC – average total organic content /in weight %)

HI – average Hydrogen index (mg HC/g TOC

f - fractional conversion (0 – completely immature organic matter; 1 – fully mature organic matter), determined on measured vitrinite reflectance

The formula applies to the calculation of oil generation. For oil expulsion to occur, a threshold volume of generated oil must be reached, i.e. 1,9 million m³ of oil per km³ of source rock. Upon reaching this threshold, the expulsion efficiency of oil is approximately 50%. In the early stages of oil generation, this threshold was not reached, meaning that primary migration of oil from the Central Carpathian Paleogene Basin (CCPB) and Lower Miocene source rocks did not occur.

Expelled oil volume = generated oil volume x expulsion efficiency

The general efficiency of secondary migration and accumulation in geological regions typically ranges from 10 to 20% (a value of 15% was applied here).

Accumulated oil volume = expelled oil volume x secondary migration and accumulation efficiency

In the oil generation window of the Lipany-1 well, the threshold values were reached or slightly exceeded. In contrast, at the Prešov-1 well, these thresholds were not attained (Table 3).

Tab. 3: Estimation of the prospective oil resources in the Lipany-1 and Prešov-1 wells. Well

Well	Lipany-1	Prešov-1
Conversion constant (k)	0.7	0.7
TOC – total organic carbon (wt.%)	0.45	0.41
HI – initial hydrogen index (mg/g)	300	240
Fractional conversion (f)	0.9	0.7
Oil generation (10 ⁶ . m ³)	3.24	1.84*
Efficiency of primary migration (50%)	1.62	–
Efficiency of secondary migration (15%)	0.243	–
Total volume of oil generated (10 ³ . m ³)	243	–

* the threshold value was not reached.

Under the given conditions, gas generation in both of the mentioned areas is quantitatively negligible, amounting to only a few thousand cubic meters of gas.

The development of hydrocarbon generative windows for the Lower Miocene and CCPB sediments in the NE part of the East Slovak Basin is presented in Fig. 14.

The geochemical characteristics of the quantitative and qualitative parameters of organic matter, as well as the extent of thermal conversion of kerogen into hydrocarbons, are presented in Figs. 15a and 15b. The data are derived from Pereszlényi et al. (1996, 2002) and Milička & Pereszlényi (2005).

Based on the trends of the individual analyzed parameters shown in Figs. 15a and 15b, the total organic carbon (TOC) content and its quality (kerogen type) in both Lower Miocene and CCPB sediments are roughly comparable, despite some relatively higher analytical values currently observed in the Lower Miocene sediments (TOC, S₂, HI). In neither case do these values represent the initial levels of these parameters, as part of

the organic matter has already been consumed over geological time. The Paleogene sediments having lost a greater proportion of their potential.

The CCPB sediments reached the onset of oil generation at the Eocene–Oligocene boundary (Lipany-1 well area), whereas the CCPB and Lower Miocene sediments in the Prešov-1 well area reached this stage of transformation only by the end of the Carpathian or the beginning of the Lower Badenian (Figs. 10 and 11).

Based on modeling and measured vitrinite reflectance (R_o), the CCP sediments reached the active stage of oil generation at the end of the Oligocene (R_o ~ 1%). From that time, following uplift up to the present, this stage has become largely passive. The Lower Miocene sediments attained the active stage of early oil generation (R_o ~ 0.6%).

The basement of both CCPB and Lower Miocene sediments (Triassic of the Krížna nappe) occur currently in the gas-generating stage (R_o = 2 - 4%) and, considering the present burial depths, is in a passive (relict) stage, with most of the hydrocarbon potential having been realized in the original sedimentary area.

4.3 Correlation of Merník asphalt with potential petroleum source rocks

As indicated by the overall geochemical characteristics of the natural asphalt from the Merník locality, it represents altered organic matter derived from Paleogene sediments, which underwent oil generation during the Early and Middle Miocene under the influence of thermal energy from the intrusive complex and hydrothermal processes. Subsequently, the volatile and soluble components were almost completely removed during the Late Miocene and Pliocene.

This is reflected in the obtained chromatographic record of the extract (Fig. 8), which also demonstrates a high degree of biodegradation, with the original n-alkanes and isoprenoids nearly entirely removed and unresolved. In the right side of the chromatogram, however, a cluster of hydrocarbons is observed, containing biomarkers that are more resistant to degradation and were used for correlation purpose

These correlations are primarily based on the comparison of triterpane distributions (m/z 191; Fig. 16) and sterane distributions (m/z 218; Figs. 9 and 17). The comparison involved the extract of the asphalt sample from Merník and sediments of the Central Carpathian Paleogene Basin (CCPB) in the Levoča Mountains area, where intensive studies of the hydrocarbon potential of this region had been conducted (Pereszlényi et al., 1996, 2002) and provided sufficient sample material.

The focus of the research in the Levoča Mountains (CCPB) was primarily on identifying petroleum sources, particularly in the vicinity of the Lipany wells. Both routine and special organic-geochemical methods were applied to samples of crude oils and potential Paleogene source rocks as well as underlying Mesozoic formations. The studies demonstrated a positive match between the oils from the Lipany wells and the Paleogene source rocks at the level of triterpane (m/z 191) and sterane (m/z 218) distributions

The presence of the oleanane biomarker indicates a common

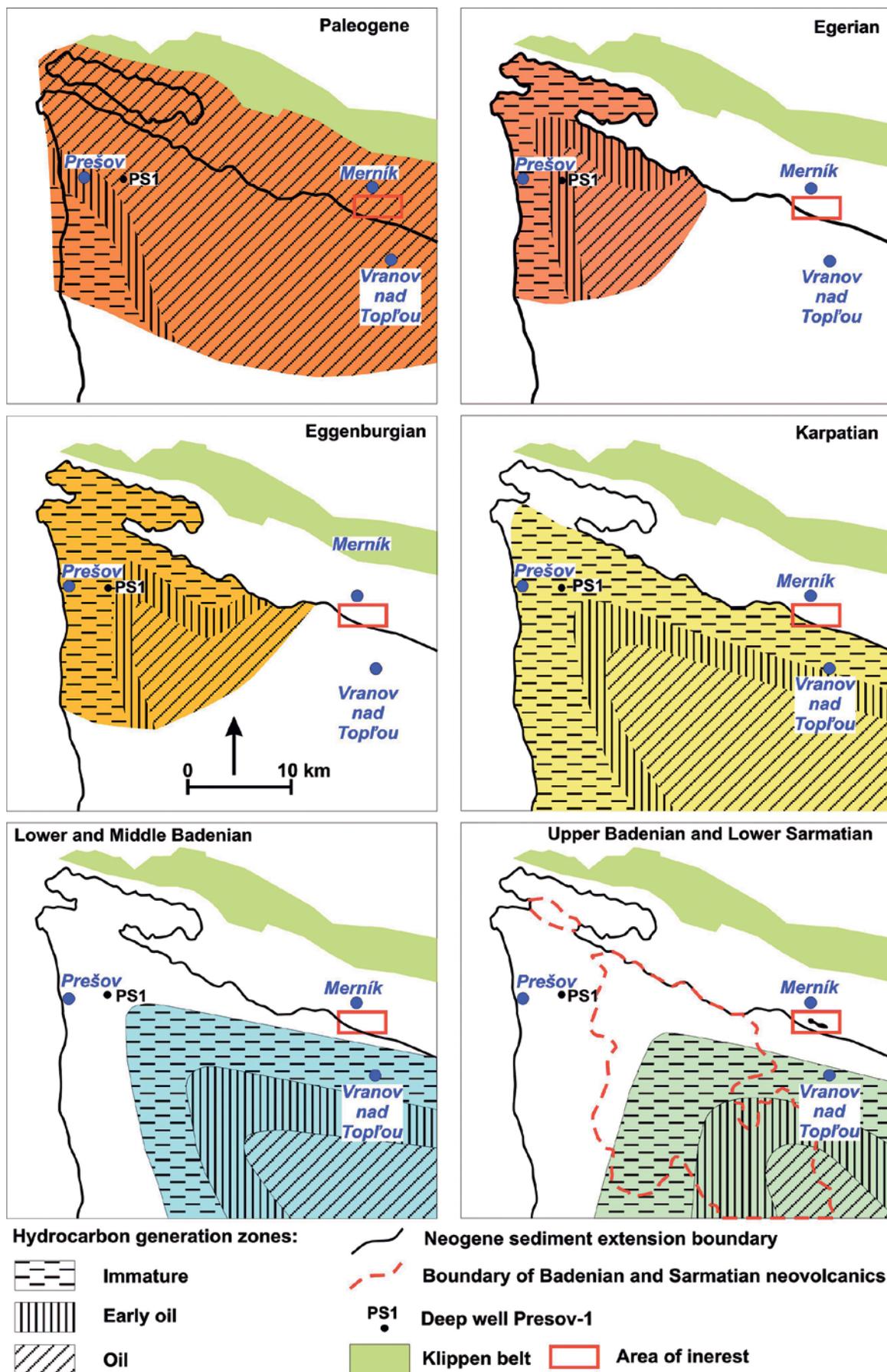


Fig. 14: NW part of East Slovak Basin - evolution of hydrocarbon generation windows in Tertiary sediments

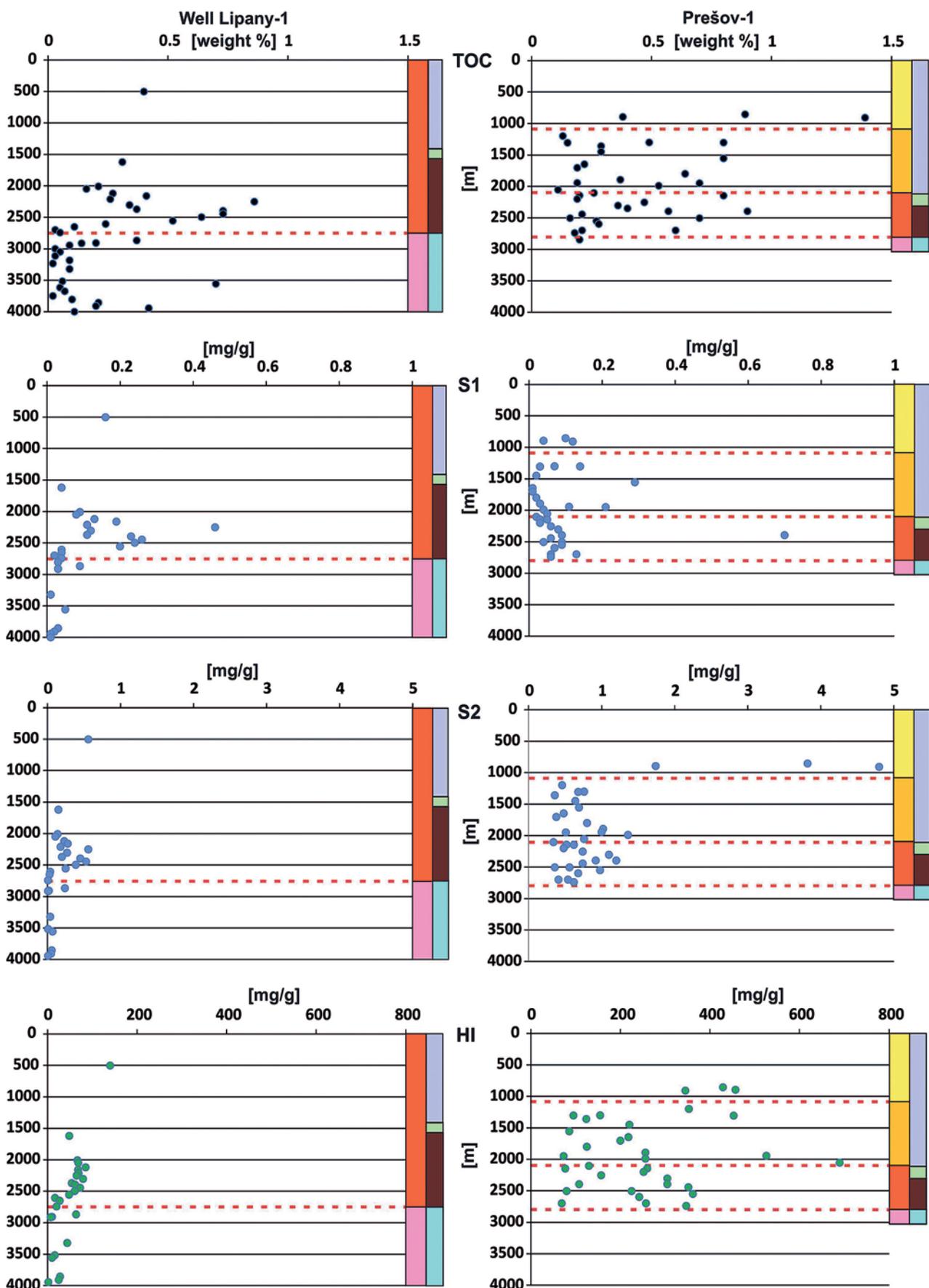


Fig. 15a: Qualitative, quantitative, and maturity parameters of organic matter in the depth profiles of the Lipany-1 and Prešov-1 wells. Legend as in Fig. 15b.

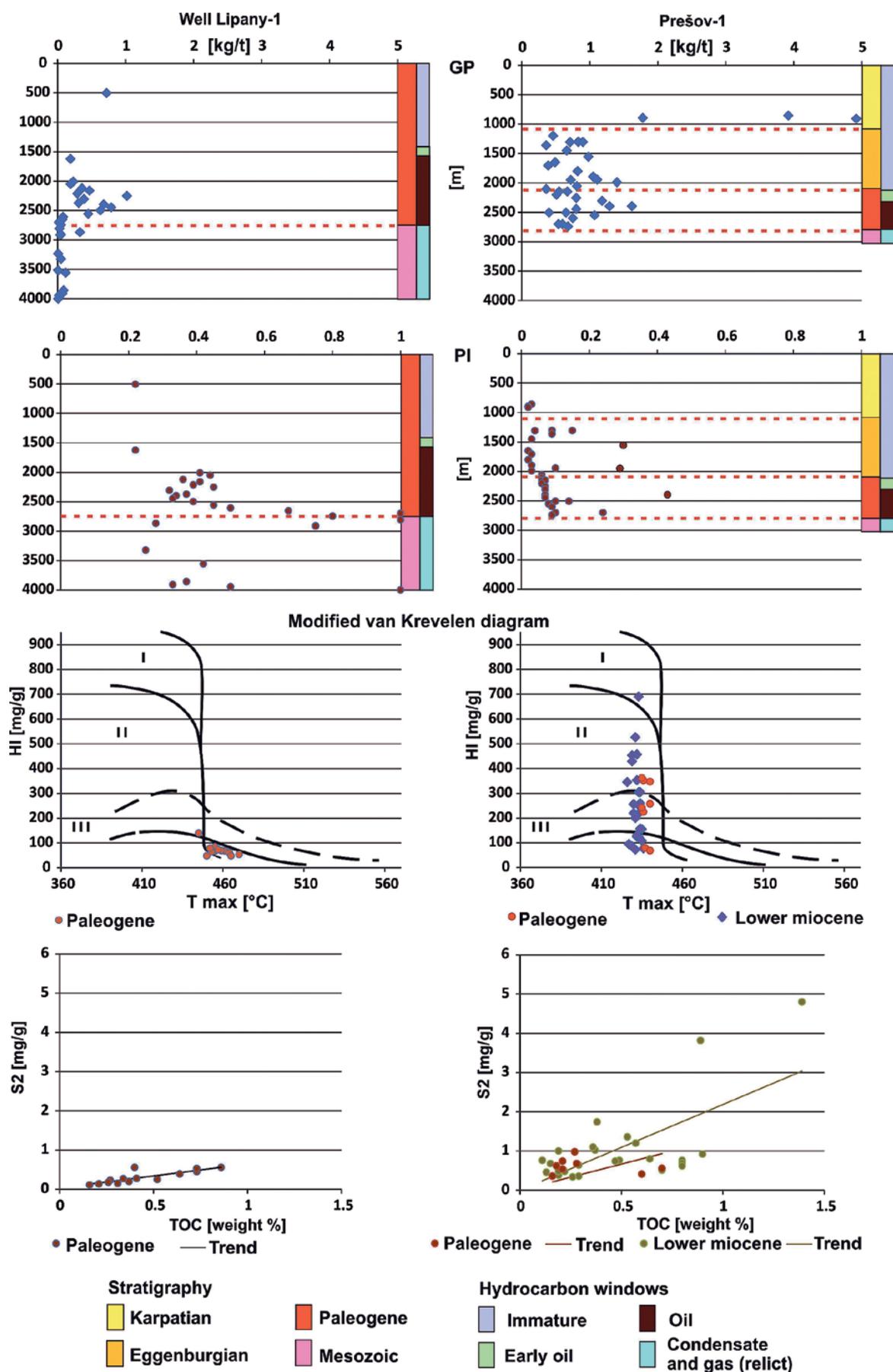


Fig. 15b: Qualitative, quantitative, and maturity parameters of organic matter in the depth profiles of the Lipany-1 and Prešov-1 wells.

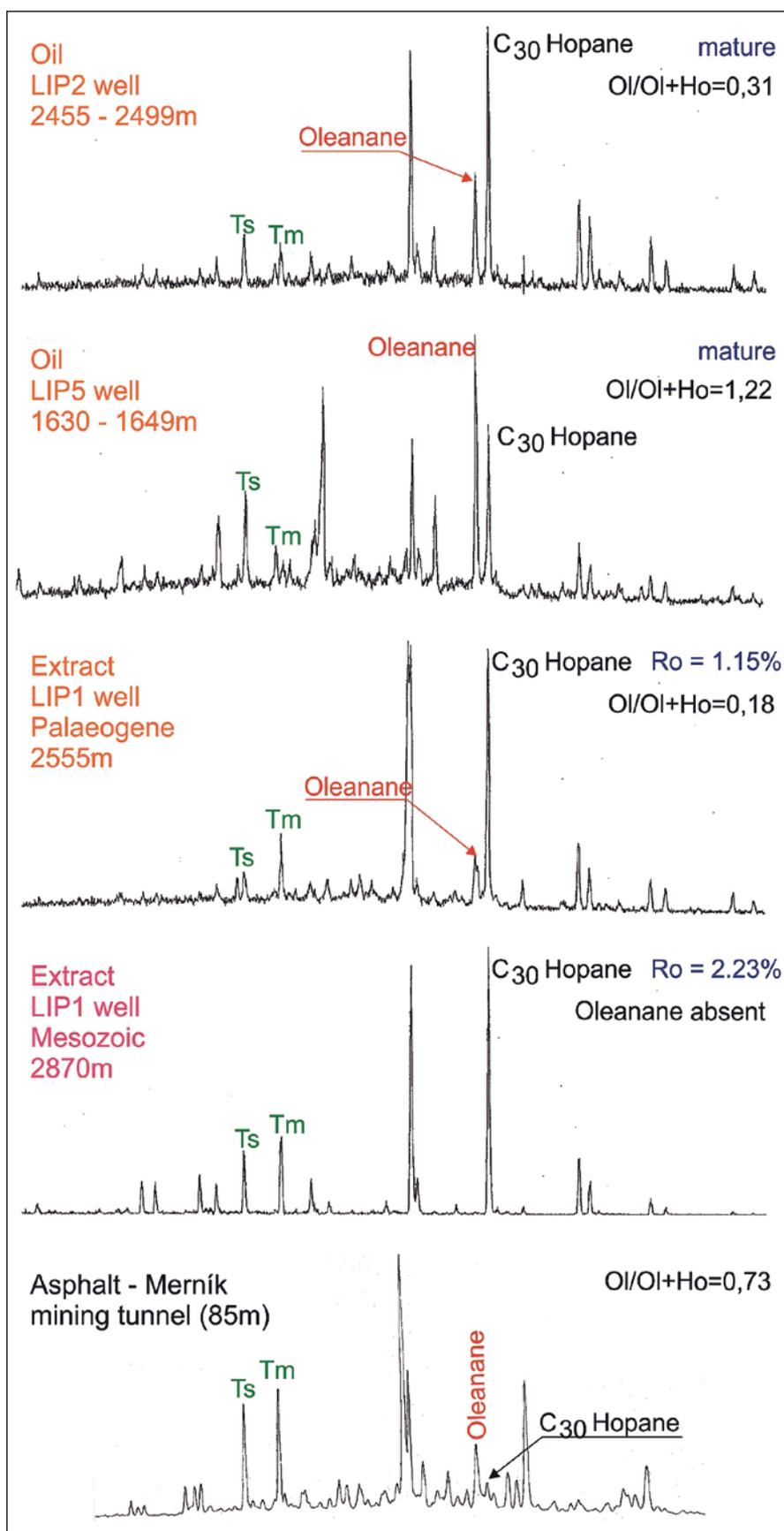


Fig. 16: Distribution of triterpanes (m/z 191) in Palaeogene oils and source rocks extract compared with Merník asphalt extract. LIP: oil wells in Lipany area (Central Carpathian Paleogene Basin); Ts: 18 α (H)-22,29,30 Trisnorneohopane; Tm: 17 α (H)-22,29,30 Trisnorhopane; OI – oleanane; Ho – C₃₀ hopane.

Tertiary petroleum source, whereas the underlying Mesozoic rocks (Triassic, Križna nappe) do not contain it at all (Fig. 16; Table 1). As further shown in the figure, the Merník asphalt sample also contains a significant amount of oleanane (oleanane index = 0.73).

Similarly, the sterane distribution in the ternary diagram (Fig. 17) points to a genetic affinity between the Lipany oils, the Paleogene source rocks, and the Merník asphalt (position of points within the dashed circle). The Mesozoic extract is shifted more toward a marine source, while the Paleogene extracts labeled LVH9 and JH in Fig. 17 show an increased contribution of terrestrial (coaly) organic matter.

5. CONCLUSIONS

Based on previous studies, it can be concluded that the northeastern part of the East Slovak Basin (specifically, the Prešov sub-basin) is an area with very low prospectivity for hydrocarbon exploration. The Mesozoic basement lost its hydrocarbon potential prior to the deposition of the Tertiary sediments, and related to the current burial depths, no active hydrocarbon generation can be expected.

Within the Tertiary sedimentary fill, the Paleogene (CCPB) sediments and, to a lesser extent, the Lower Miocene sediments exhibit a certain but generally low hydrocarbon potential based on organic matter analyses. This is consistent with the occurrence of small oil accumulations in the Lipany-1 well area, with reserves in order of a few thousand cubic meters.

In the Merník area, no significant oil accumulations are known, indicating that primary migration of oil from the source rocks did not occur. The only exceptions are minor asphalt accumulations, which formed as a result of elevated temperatures during volcanic activity. The presence of natural asphalt and organic minerals only within the extent of

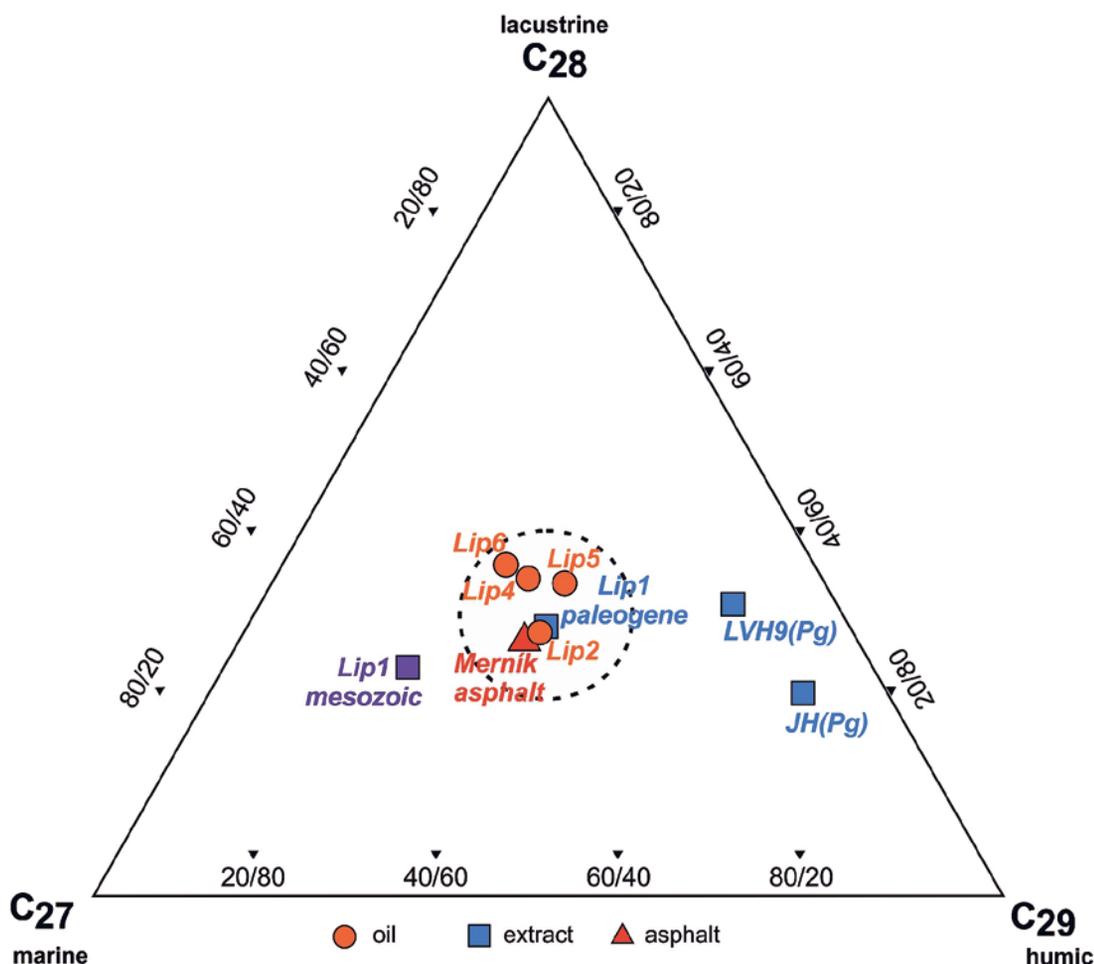


Fig. 17. Ternary diagram of C27-28-29 steranes in Palaeogene oils and source rocks extracts compared with Merník asphalt extract. LIP – oil wells in Lipany area (Central Carpathian Paleogene Basin); LVH and JH hydrogeological wells in the same area.

the Paleogene sediments indicates that the organic matter of these sediments was the primary, and likely the only source of their formation.

Based on modeling and the evaluation of geochemical measurements (Rock-Eval pyrolysis, microphotometry), only the Paleogene CCPB sediments in the adjacent area reached the stage of active oil generation.

The source of natural asphalt at the Merník mercury deposit is the organic matter of the CCPB sediments, as evidenced by the genetic affinity of biomarkers observed in oils and Paleogene source rocks in the Lipany area and in the Merník asphalt itself.

The oil generated by these sediments, which is still present in the Lipany area at depths exceeding 1600 m, has so far undergone minimal degradation. In contrast, in the Merník area, natural asphalt occurs under near-surface conditions at depths on the order of a few hundred meters. Under these conditions, during migration from greater depths, the volatile components were lost, and the material underwent significant biodegradation, leaving only the heavy, asphaltic fractions.

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